An Integrative Monitoring and Modeling Program of the Environmental Response to Changing Mercury Deposition to North America

Robert P Mason
Marine Sciences Department
University of Connecticut
Groton, CT 06340

This presentation is made on behalf of a cast of many whose contributions are all acknowledged and appreciated

Why do we need to monitor mercury in the environment?

- **The concentration of mercury (Hg) in the environment has been significantly increased by anthropogenic inputs and elevated levels of methylmercury (MeHg) in fish is an important human health and environmental concern**
- **Regulations are being mandated or implemented that are aimed at reducing risk to humans and other wildlife – what is their impact?**
- **Changes in Hg deposition to aquatic ecosystems are likely occurring due to voluntary or mandated changes in anthropogenic emissions**
- **The impacts of such changes on MeHg levels in fish are uncertain, and the impacts are not being effectively monitored at present.**

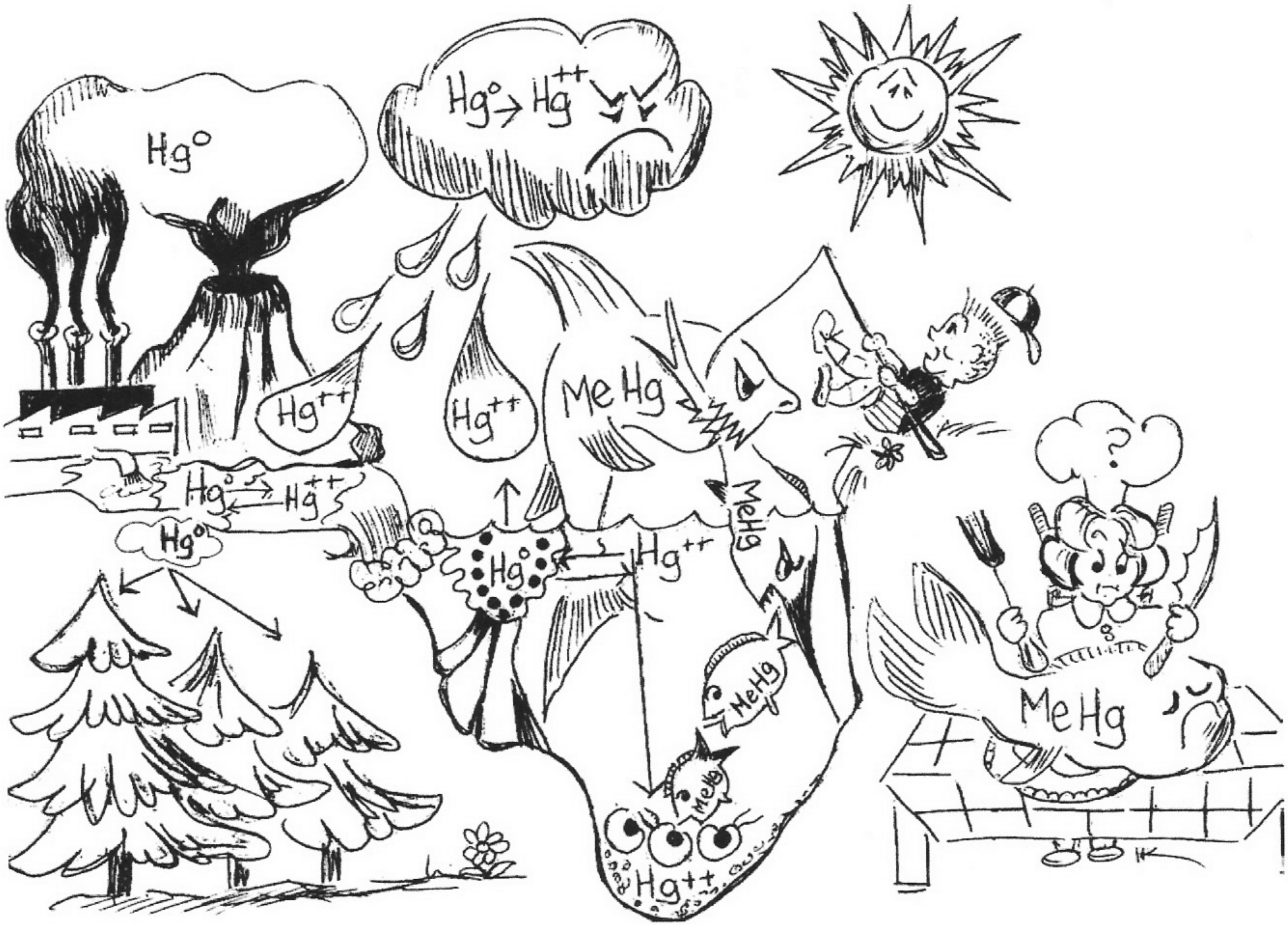
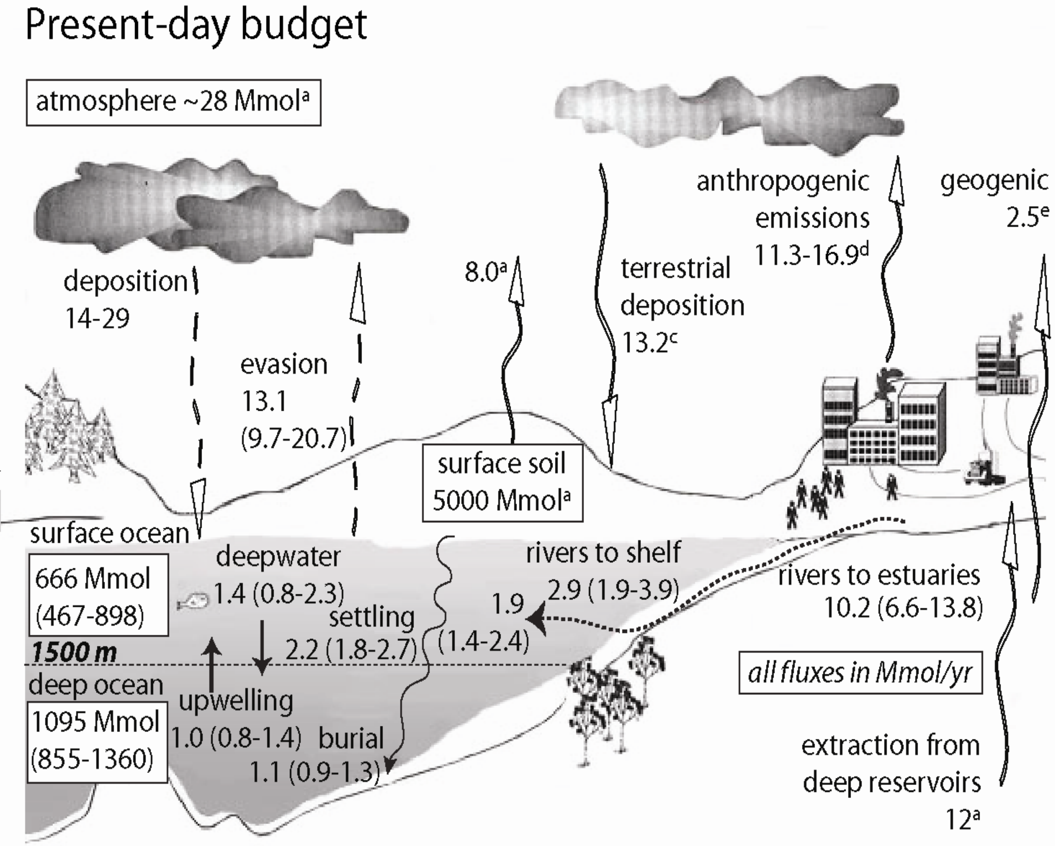
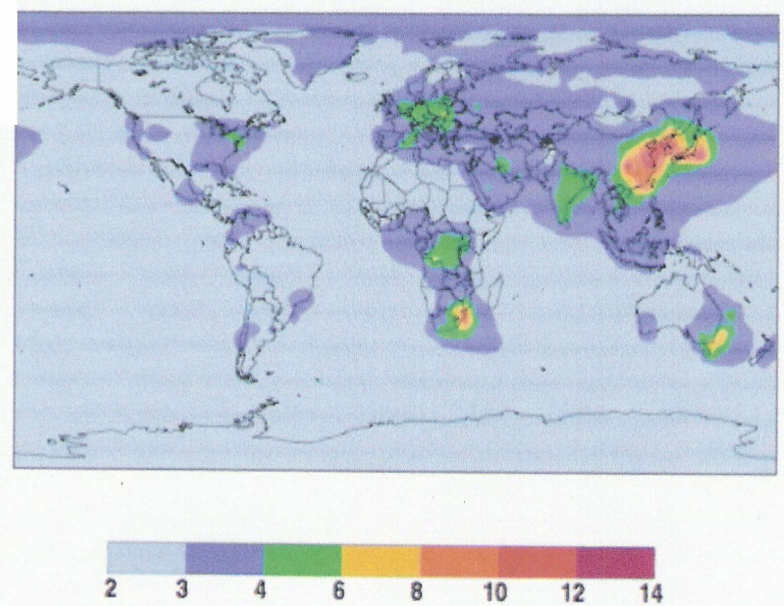


FIG. 4. The global cycling of mercury, its methylation in aquatic sediments and the bioaccumulation of methylmercury in aquatic food chains to eventually enter the human diet (from Fitzgerald and Clarkson, 1991 and Mason et al., 2005).



Box and computer models suggest that anthropogenic inputs have increased by at least a factor of 3 globally (range 2-10 regionally). In some regions emissions may be decreasing, while in other locations they are increasing.



But how are aquatic systems and levels of MeHg in fish changing? Is the response linear?

Sunderland & Mason (2007)
Selin et al., in rev.

Developing a Monitoring and Modeling Network: Current Initiatives and Projected Approaches

Workshop in Florida, September 2003

1) Who was there?

- Approx. 30 mercury researchers, from academia, government, NGO's and industry. Meeting organized by SETAC, with initial funding from EPA, EPRI and others

2) Why do this?

- Existing mercury monitoring programs are not integrated and only provide information about specific sites or areas
- Assessing the effectiveness of control programs is important both in terms of environmental protection and good policy development

3) What was the purpose?

- Select a set of indicators that reflect the best scientific judgment about what should be monitored
- Design a mercury monitoring strategy that is capable of assessing changes in mercury in all compartments of the environment as a result of changes in emissions
- Strategy that is realistic and builds off of existing monitoring efforts

The Products

Publications

1. Mason, R.P., Abbott, M.L., Bodaly, R.A., Bullock Jr., O.R., Driscoll, C.T., Evers, D., Lindberg, S.E., Murray, M., and Swain, E.B. 2005. Monitoring the Response to Changing Mercury Deposition. Environ. Sci. Technol., 39 (1): 14A-22A, January 1, 2005

2. Harris, et al. 2007. Ecosystem Responses to Mercury Contamination: Indicators of Change. SETAC Press: Pensacola, FL, 2007

Briefings and Presentations

House and Senate staff, December 2004
EPA, other Federal, Feb and winter 2005
Heinz Center Meeting, Aug 2007
Presentations at International Mercury Meetings
Presentations at NADP and other meetings
April 2008 Meeting in preparation

Bills?

Draft Bill in Congressional Committees
House, Allen, sponsor; Senate, Clinton, sponsor

Goal is to support implementation of a national mercury monitoring program to assess the effects of reducing mercury emissions on the U.S. environment

....
(Original Signature of Member)

110TH CONGRESS
1ST SESSION

H. R. ____

To provide for the establishment of a national mercury monitoring program.

IN THE HOUSE OF REPRESENTATIVES

Mr. ALLEN introduced the following bill; which was referred to the Committee on ______________________

A BILL

To provide for the establishment of a national mercury monitoring program.

Be it enacted by the Senate and House of Representatives of the United States of America in Congress assembled,

SECTION 1. SHORT TITLE.

This Act may be cited as the "Comprehensive National Mercury Monitoring Program Establishment Act".

SEC. 2. FINDINGS.

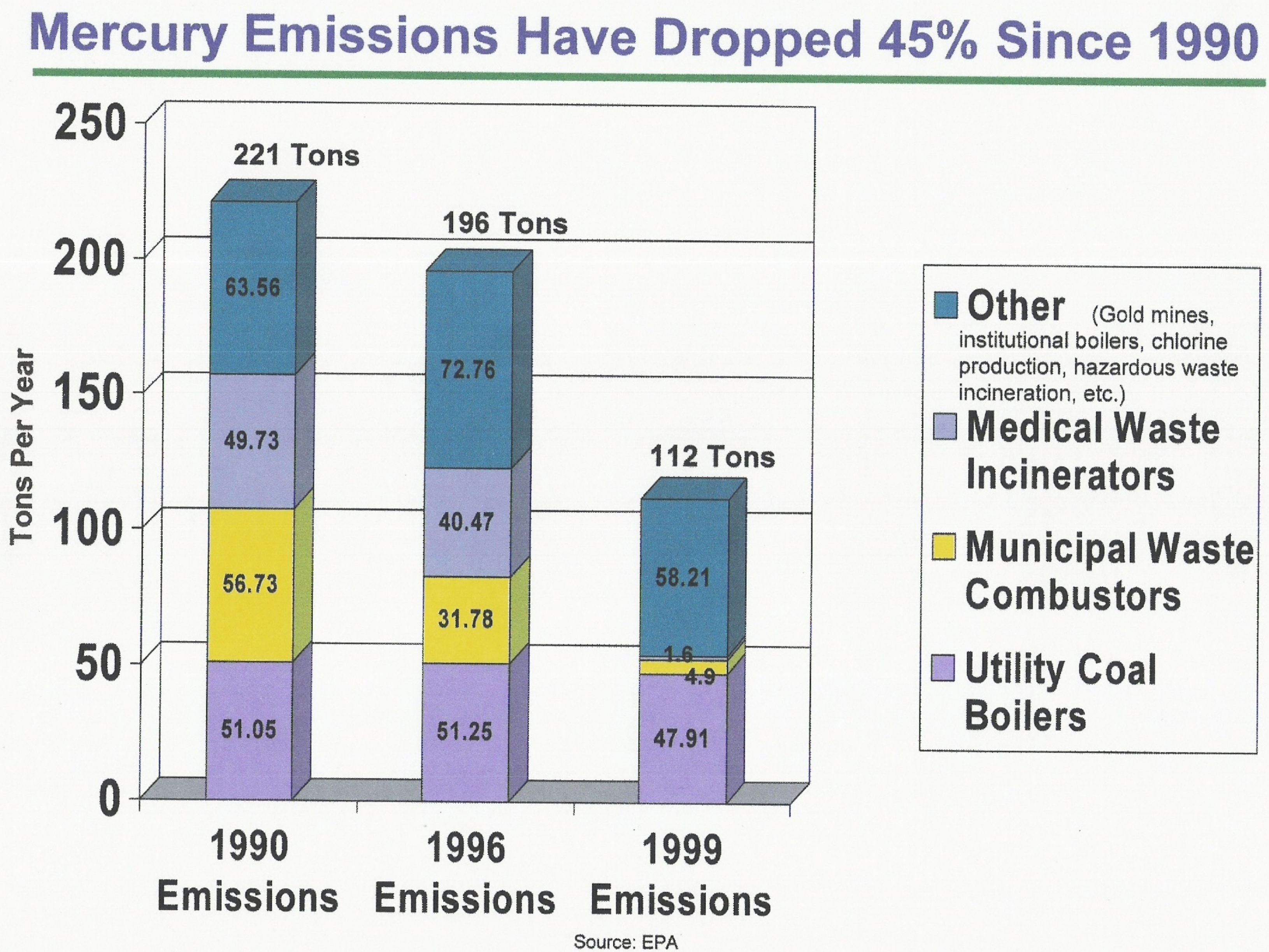
Congress finds the following:

(1) Mercury is a potent neurotoxin of significant ecological and public health concern. Exposure

Comprehensive National Mercury Monitoring Program Establishment Act

1. Involves all relevant Federal agencies (EPA, FWS, USGS, NOAA, NPS and FS)
2. Sets out the framework and refers to the publications for guidance
3. Appoints a Science Advisory Committee
4. Discusses costs and their distribution

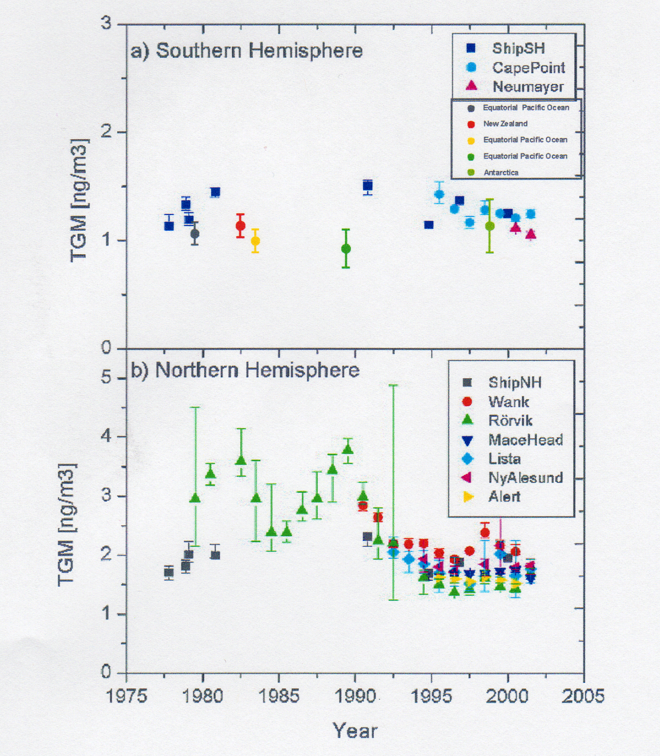
In the USA…

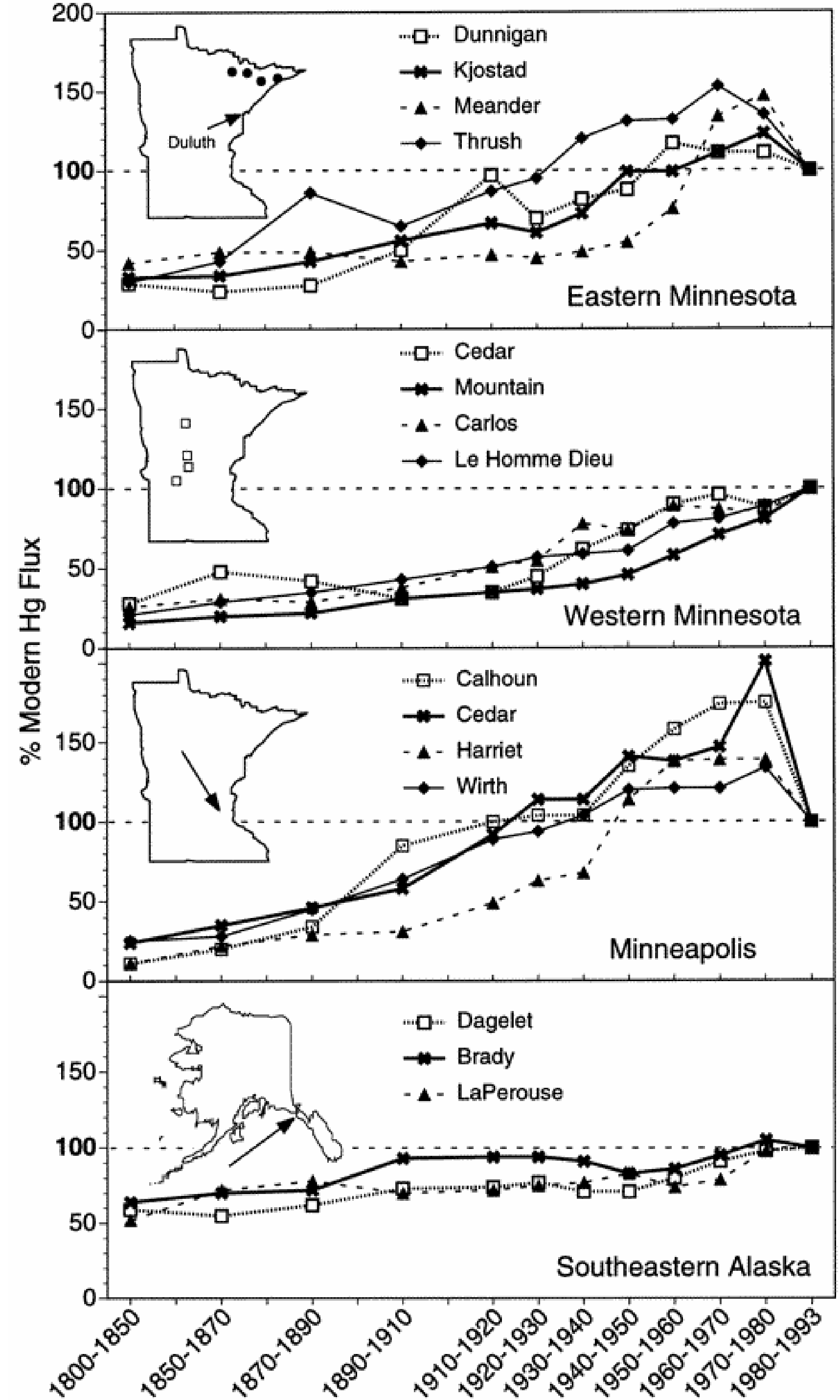


From EPA Webpage

Is Mercury Deposition Changing?

What is the Impact on Ecosystems?





Airsheds and Watersheds 35

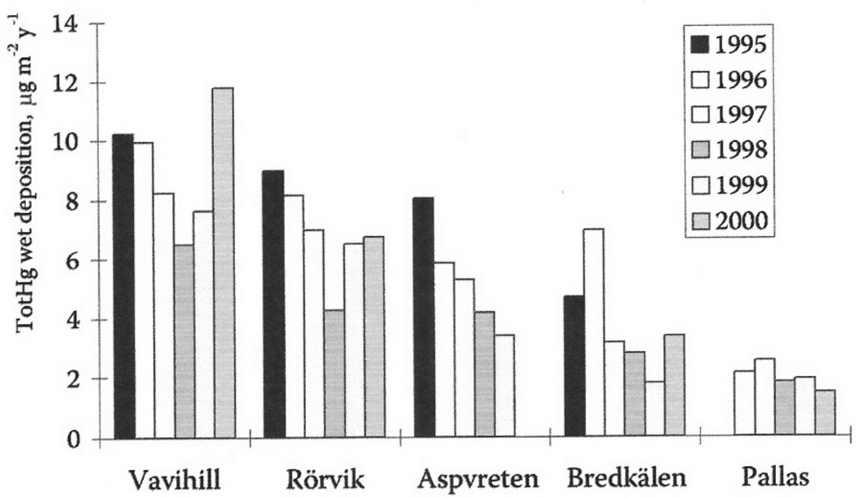
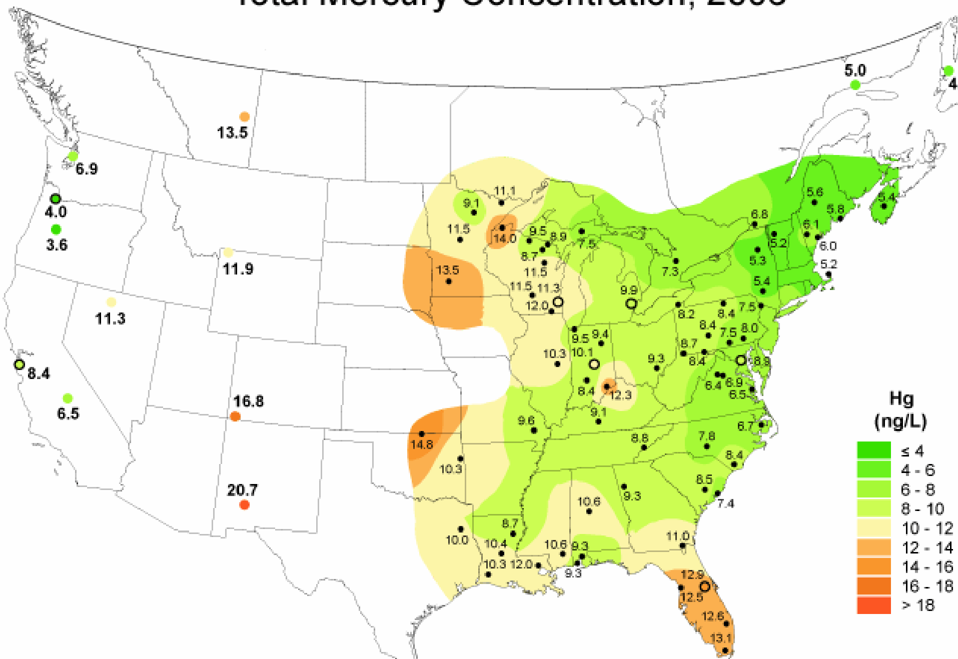


FIGURE 2.6 Wet deposition of THg over a south to north gradient in Sweden and Finland. Vavihill (southernmost) and Pallas (northernmost). Data are shown for 6 years.

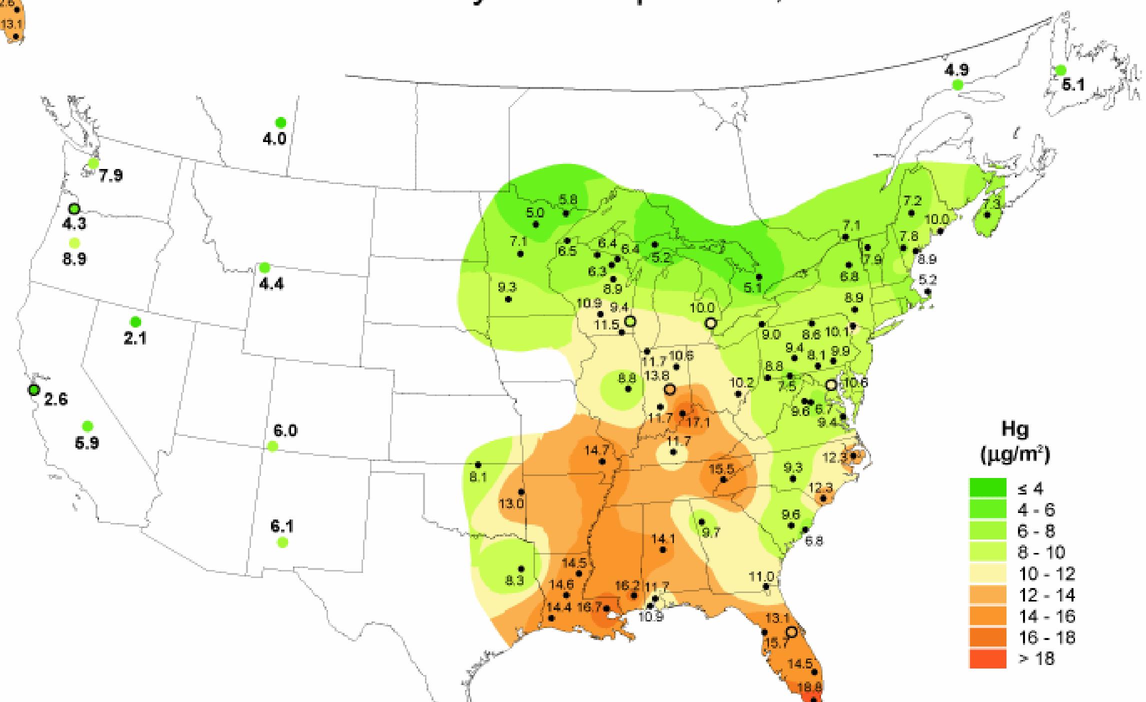
Total Mercury Concentration, 2006



National Atmospheric Deposition Program/Mercury Deposition Network

- Mercury concentrations in rain are higher on the East Coast than the West (generally)
- Fluxes are higher in the Southwest and reflect the higher rainfall amounts. Even though concentrations are higher in the arid regions, fluxes are smaller

Mercury Wet Deposition, 2006

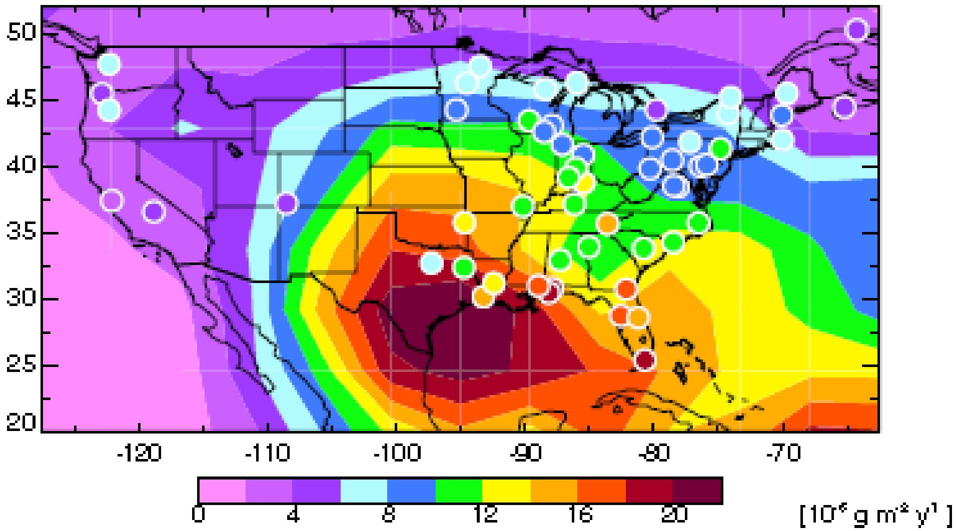


National Atmospheric Deposition Program/Mercury Deposition Network

The distribution suggests that deposition of Hg emitted in the USA is an important component to wet deposition, and this input is more important for locations on the East Coast

Information from NADP website

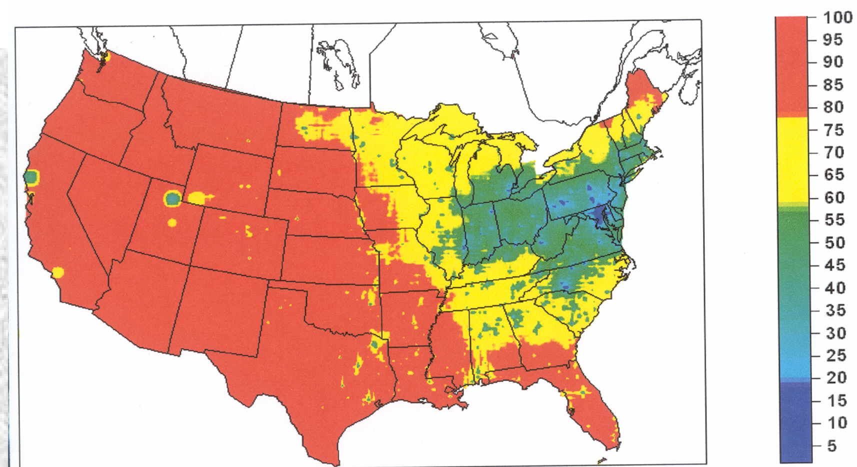
Models are becoming more sophisticated and better at predicting Hg deposition for North America



(Left) As an example, GEOS-Chem model predictions compared with MDN measurements.

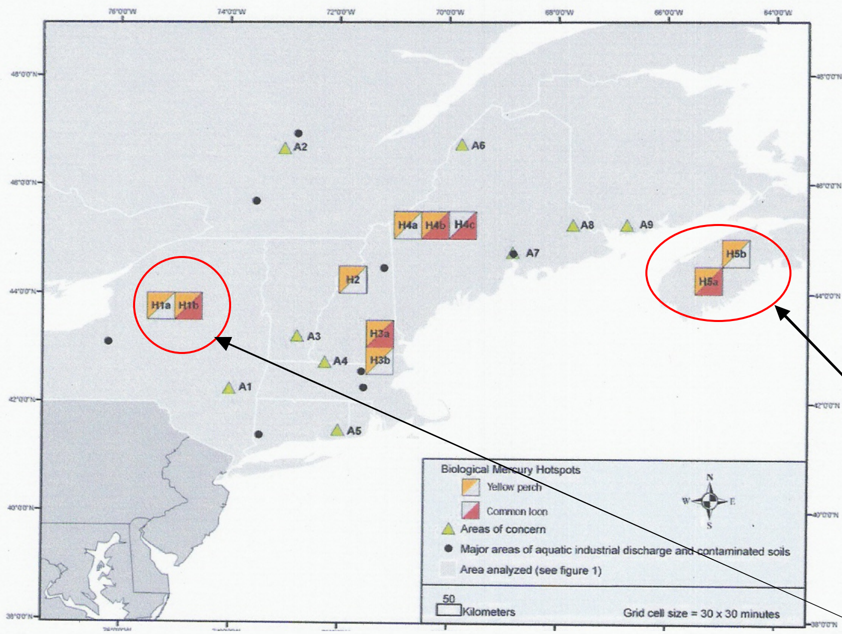
Selin et al (unpubl.)

Contribution (%) of other than U.S. Anthropogenic Sources to Hg Deposition



Source: Seigneur et al

(Right) The importance of regional compared to global sources is a function of location within the USA



BUT NOT ALL SYSTEMS RESPOND IN THE SAME WAY

Regions with elevated Hg levels in fish and birds are indicated (so-called "hotspots"). Also noted are "areas of concern" with somewhat elevated levels. The table indicates the potential reasons for the elevated levels – either elevated deposition or watershed "sensitivity"

Table 3. Hypothesized mechanisms for presence of biological mercury (Hg) hotspots in the Northeast.

		Hypothesized mechanisms of Hg contamination				
Biological Hg hotspot	**State/ province**	**Regional and global atmospheric deposition**	**Water-level management**	**Landscape sensitivity**	**Local air emissions**	**Local soil contamination**
H1a: Adirondack Mountains (west)	New York	x	–	x	–	–
H1b: Adirondack Mountains (central)	New York	x	–	x	–	–
H2: Upper Connecticut River	New Hampshire, Vermont	x	x	–	–	–
H3a: Merrimack River (middle)	New Hampshire	x	–	–	x	–
H3b: Merrimack River (lower)	Massachusetts, New Hampshire	x	–	–	x	–
H4a: Upper Androscoggin River	Maine, New Hampshire	x	x	–	–	–
H4b: Upper Kennebec River (west)	Maine	x	x	–	–	x
H4c: Upper Kennebec River (east)	Maine	x	x	–	–	–
H5a: Kejimkujik National Park	Nova Scotia	x	–	x	–	–
H5b: Central Nova Scotia	Nova Scotia	x	–	x		

Evers et al. (2006)

Hammerschmidt and Fitzgerald (2007)

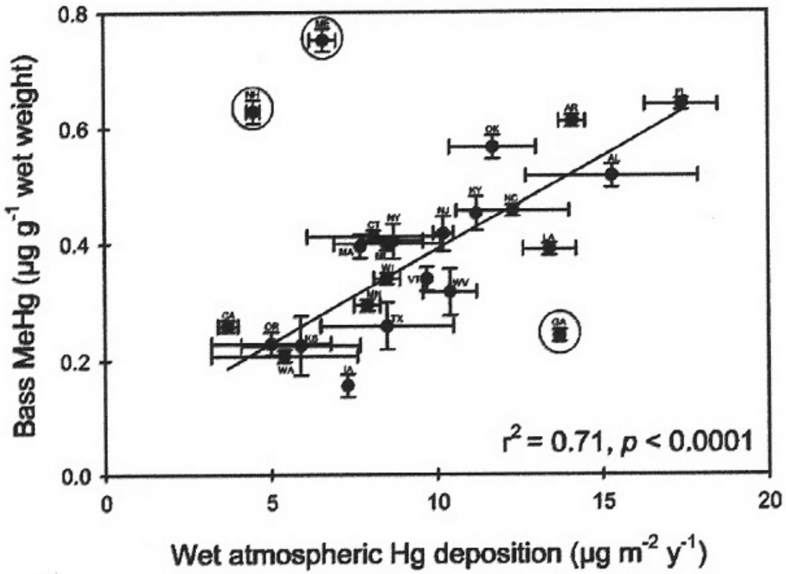
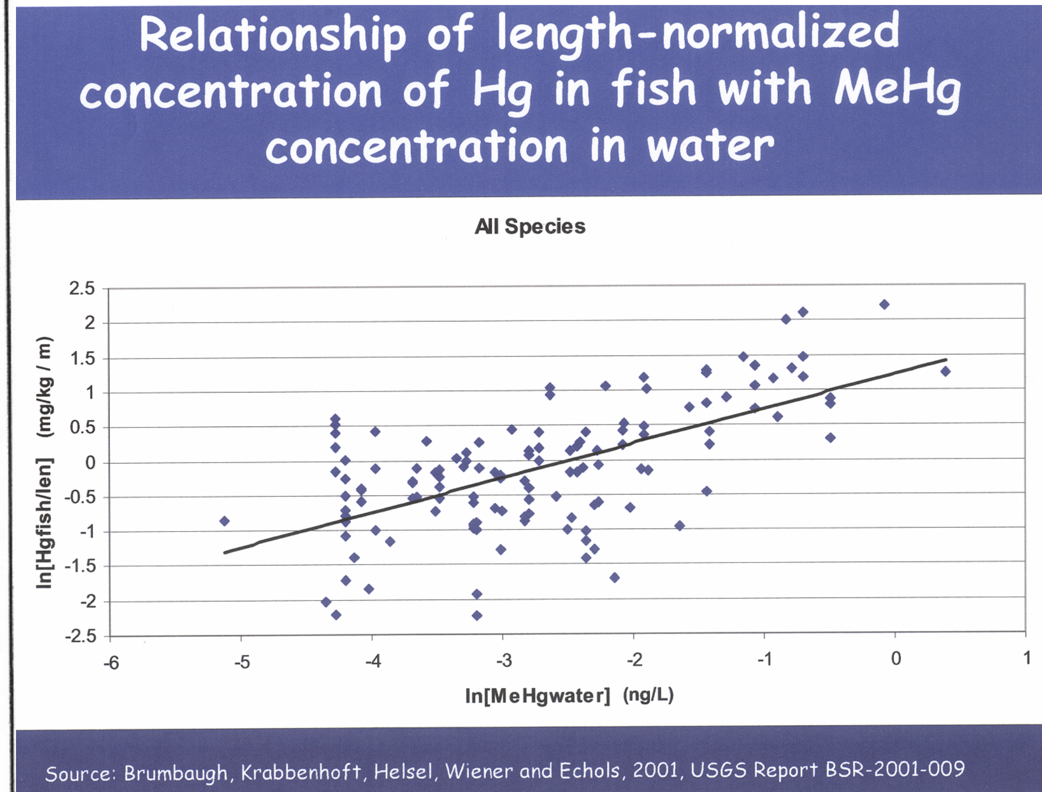
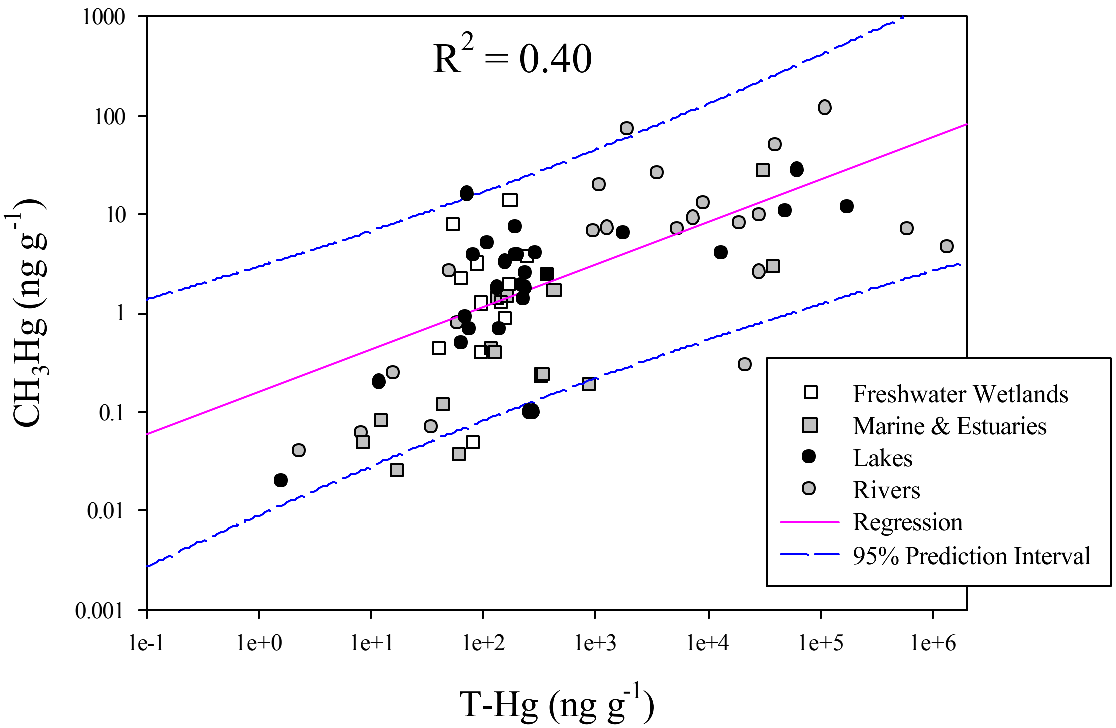


FIGURE 1. Relation between weighted-mean concentration of MeHg in fillets of largemouth bass (30−40 cm total length) and average annual wet atmospheric deposition of total Hg among 22 of 25 American states: AL, Alabama; AR, Arkansas; CA, California; CT, Connecticut; FL, Florida; GA, Georgia; IA, Iowa; KS, Kansas; KY, Kentucky; LA, Louisiana; ME, Maine; MA, Massachusetts; MI, Michigan; MN, Minnesota; NH, New Hampshire; NJ, New Jersey; NY, New York; NC, North Carolina; OK, Oklahoma; OR, Oregon; TX, Texas; VT, Vermont; WA, Washington; WV, West Virginia; WI, Wisconsin. Results for GA, NH, and ME (shown circled; see text) are not included in the regression analysis. Error bars are ± 1 SE. Mean values are distributed normally (p = 0.76) with constant variance (p = 0.83).

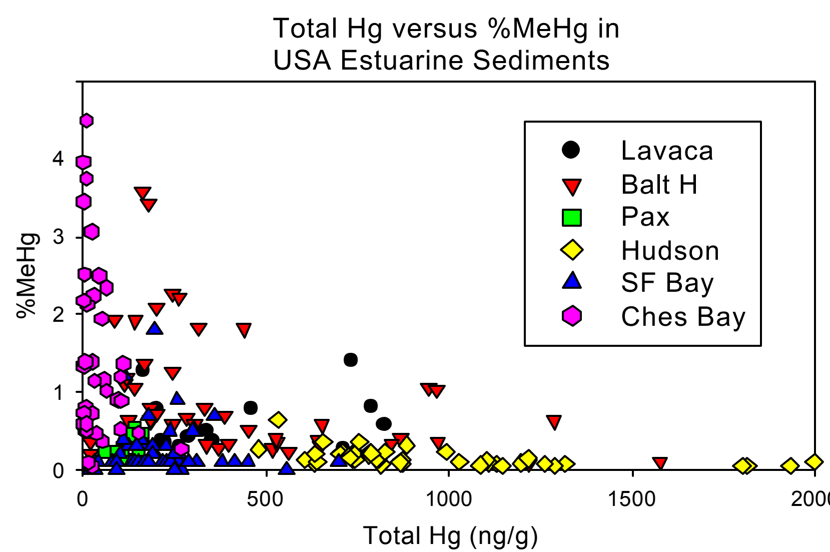


- Data shows that there is a reasonable correlation between Hg in wet deposition and Hg in fish over large scales but there is variability (up to a factor of four)
- Data shows that there is a correlation between Hg in water and Hg in fish – again, there is relatively large variability
- CONCLUSION: IT IS INSUFFICIENT TO MONITOR DEPOSITION ONLY

The fraction of total mercury that is methylmercury appears to decrease with increasing mercury concentration. Also, it is different for different types of ecosystems



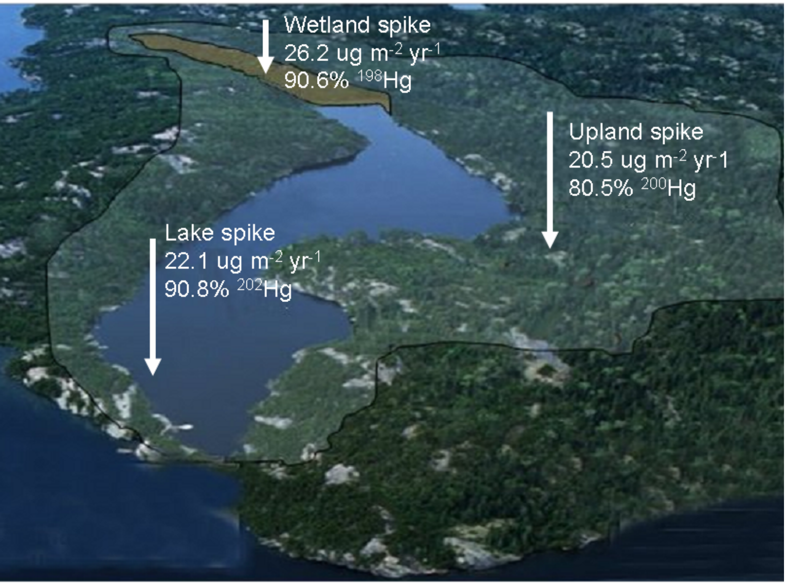
Other factors change in concert with changes in Hg inputs, especially for contaminated systems (e.g. TOC, sulfide). Many factors impact bioavailability

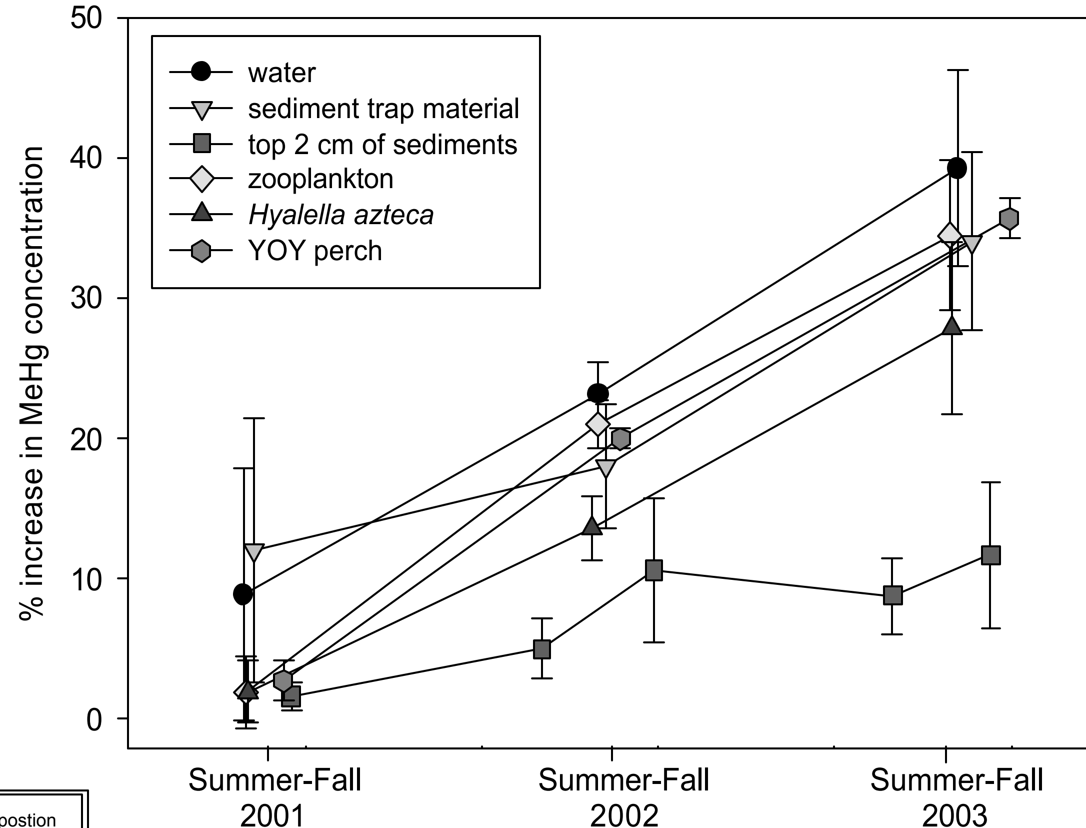


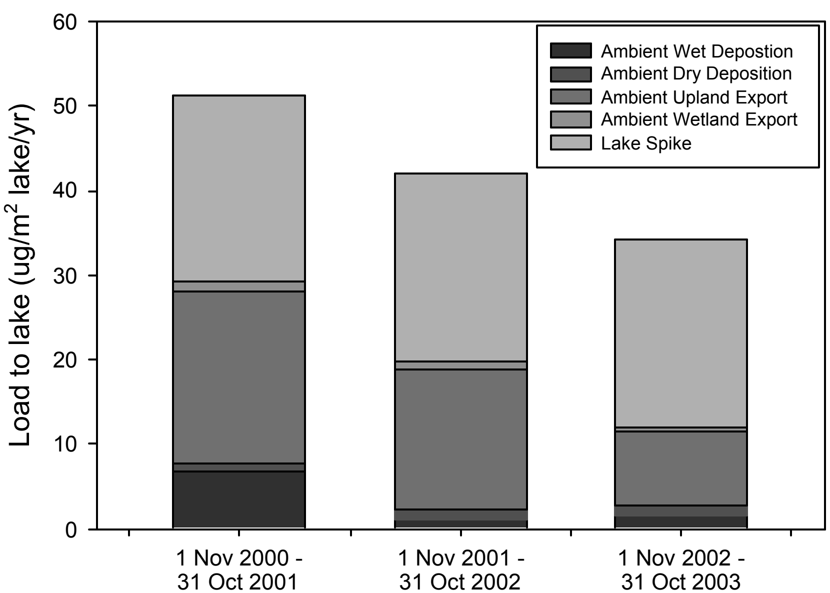
So, it is not enough to measure only deposition and other inputs…

Benoit et al. (2003)

Metaalicus Project





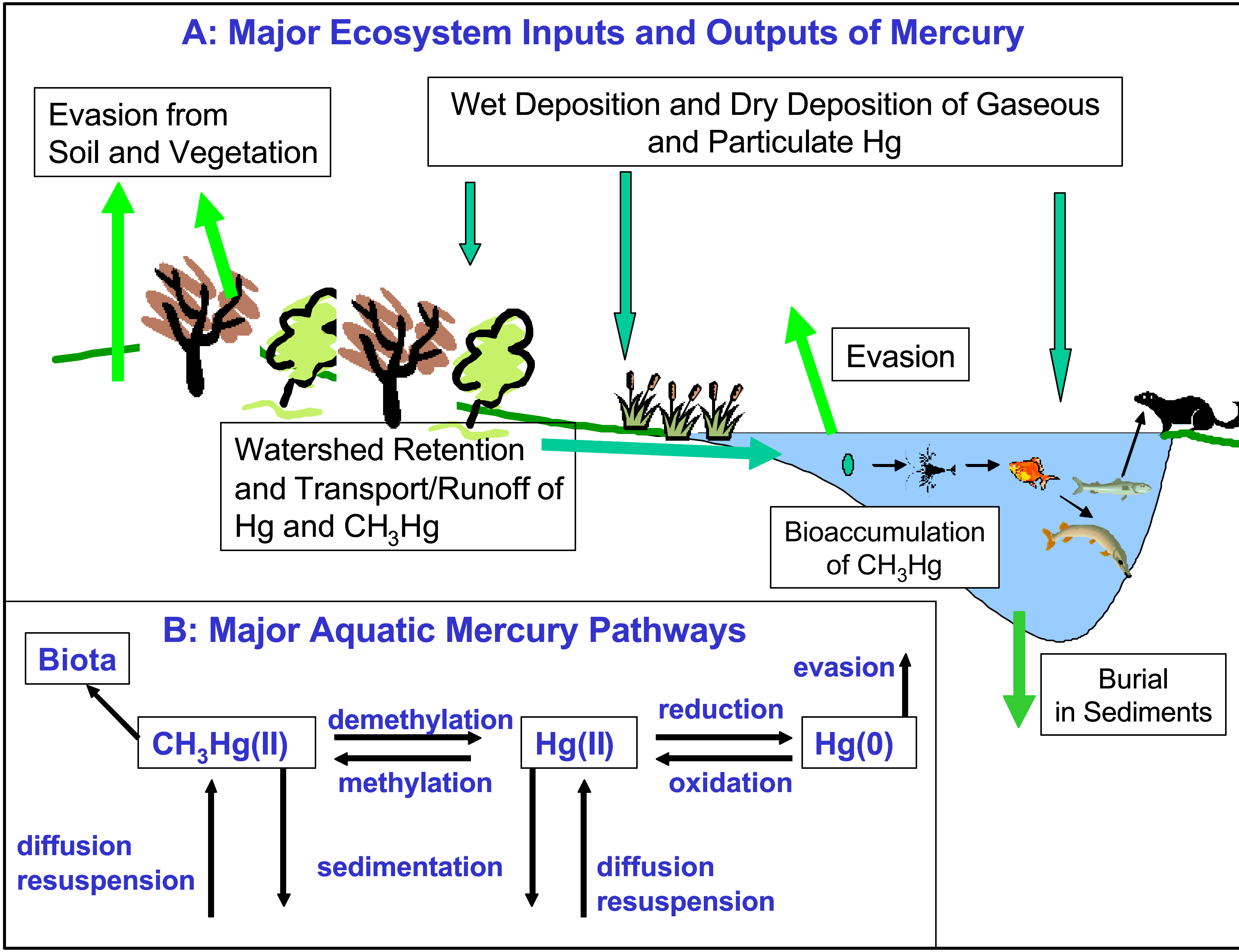


Response, almost exclusively due to the directly added Hg, was rapid and had not reached steady state after 3 years, and continues to rise with continued addition. So, these results suggest a rapid response in an ecosystem to a decrease in direct deposition to the water surface

(PNAS, Harris et al., 2007b)

An examination of mercury in lakes in Maryland (Gilmour et al., 2007) indicate that there are numerous factors besides mercury deposition that influence fish methylmerucry concentrations (this has been shown in a number of other locations)

Component Process in Hg cycle	Dependant variables assessed	Significantly correlated variables
Hg deposition, transport and accumulation in lakes	Hg in water	• Water chemistry – Cl (+), DOC (+), SO4 (+) • Landuse: % developed (+), % forested (-) • Hg deposition rates (+) • Reservoir surface area (+)
	Hg in sediment	• Sediment grain size/organic matter content • Hg in water (+) • Landuse: % developed land (+) • Hg deposition rates (+)
Net MeHg production	% MeHg in water	• pH (-) • SO4 (+) • Bottom water DO (-) • Landuse: % ag or developed land (+)
	% MeHg in sediment	• Reduced sulfide (-) • Organic matter content (+)
MeHg bioaccumulation	Bioaccumulation factors for size-normalized largemouth bass	• Dissolved oxygen in bottom water (-) • pH (+) • Lake surface:water ratio
Overall	Size-normalized Hg in largemouth bass	• MeHg in water (+) • Lake surface:water ratio • pH (-)



From Mason et al. (2005)

Considerations in Study Design

- The Source of the Change in Deposition. The detection of change in local/regional/continental deposition due to anthropogenic inputs can be confounded by changes in natural emissions or re-emission; of by changes in other parts of the globe. Multiple sites are therefore needed.
- Timing of Detecting Change. Timescales of response to changes in atmospheric deposition will differ for different metrics and are not well known, and may differ for different ecosystems. Indicators need to respond on a variety of timescales
- Site Location Differences. These need to be considered, as detailed above
- Modeling will be an important part of integration and future projection of the information obtained. Consideration needs to be given to the modeler's wants
- Indicator Criteria are needed to choose scientifically rational indicators

The Indicators

Indicators should be:

- Comparable across ecosystems
- Integrate variability in space and time
- Relatively simple to interpret
- Easy to sample, process and analyze
- Already measured or part of existing databases
- Responsive to Hg loading on a relatively short timescale
- Detect, or reflect, changes in MeHg production
- Reflect changes in exposure

Not just measuring mercury. Goal is to assess changes in mercury concentrations in important environmental "compartments"

AND

to differentiate those changes from the effects of other environmental changes (e.g. wetland destruction/restoration, sulfate deposition, etc.)

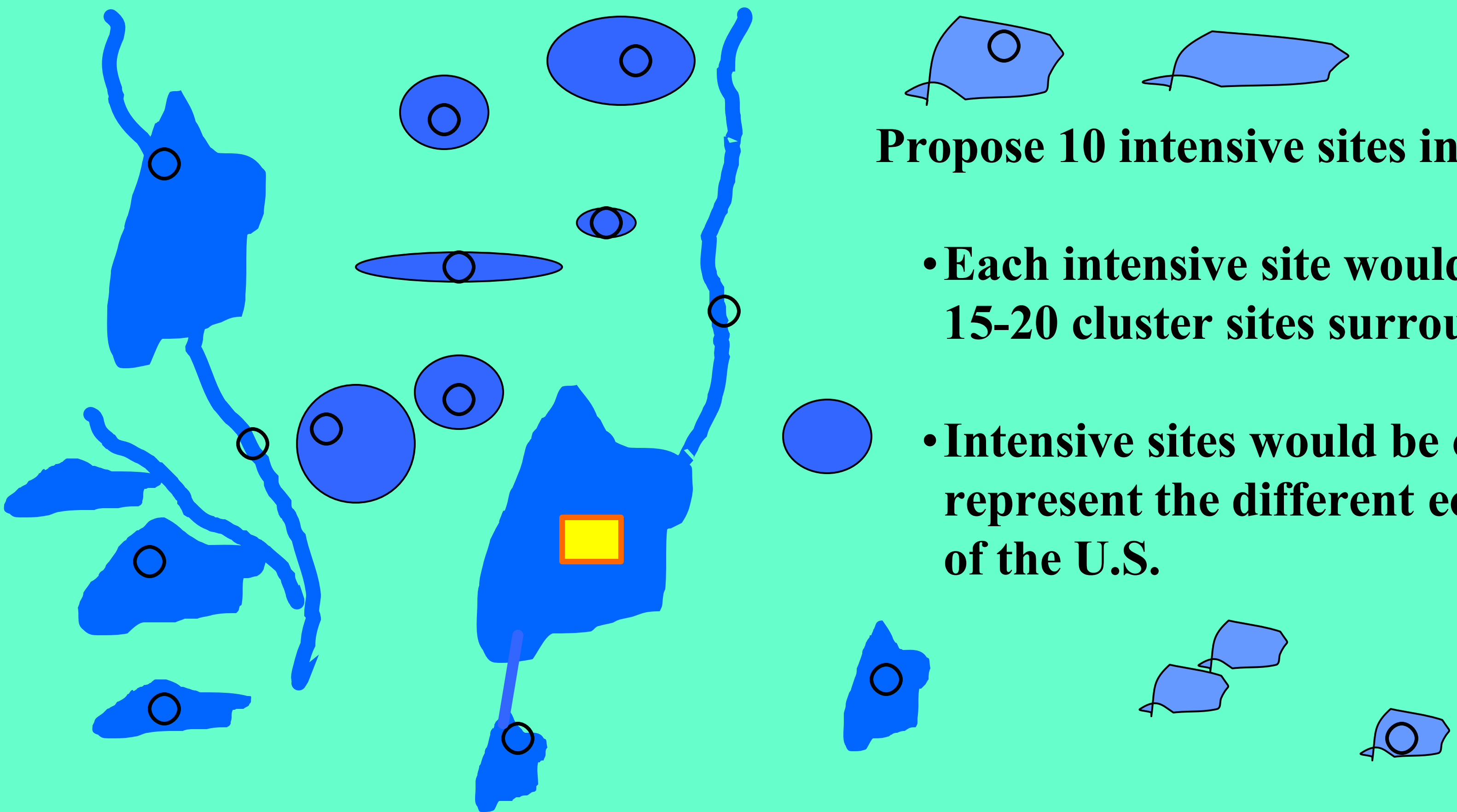
From Mason et al. (2005)

From Mason et al. (2005)

Proposed Design

Propose a combination of "intensive sites" and "cluster sites":

- **Intensive sites are those where detailed studies will be done to track changes and assess the cause of any changes**
- **Cluster sites will allow data from the intensive sites to be extrapolated to a broader area, and extrapolate results of the detailed investigations across ecosystems of similar atmospheric input**

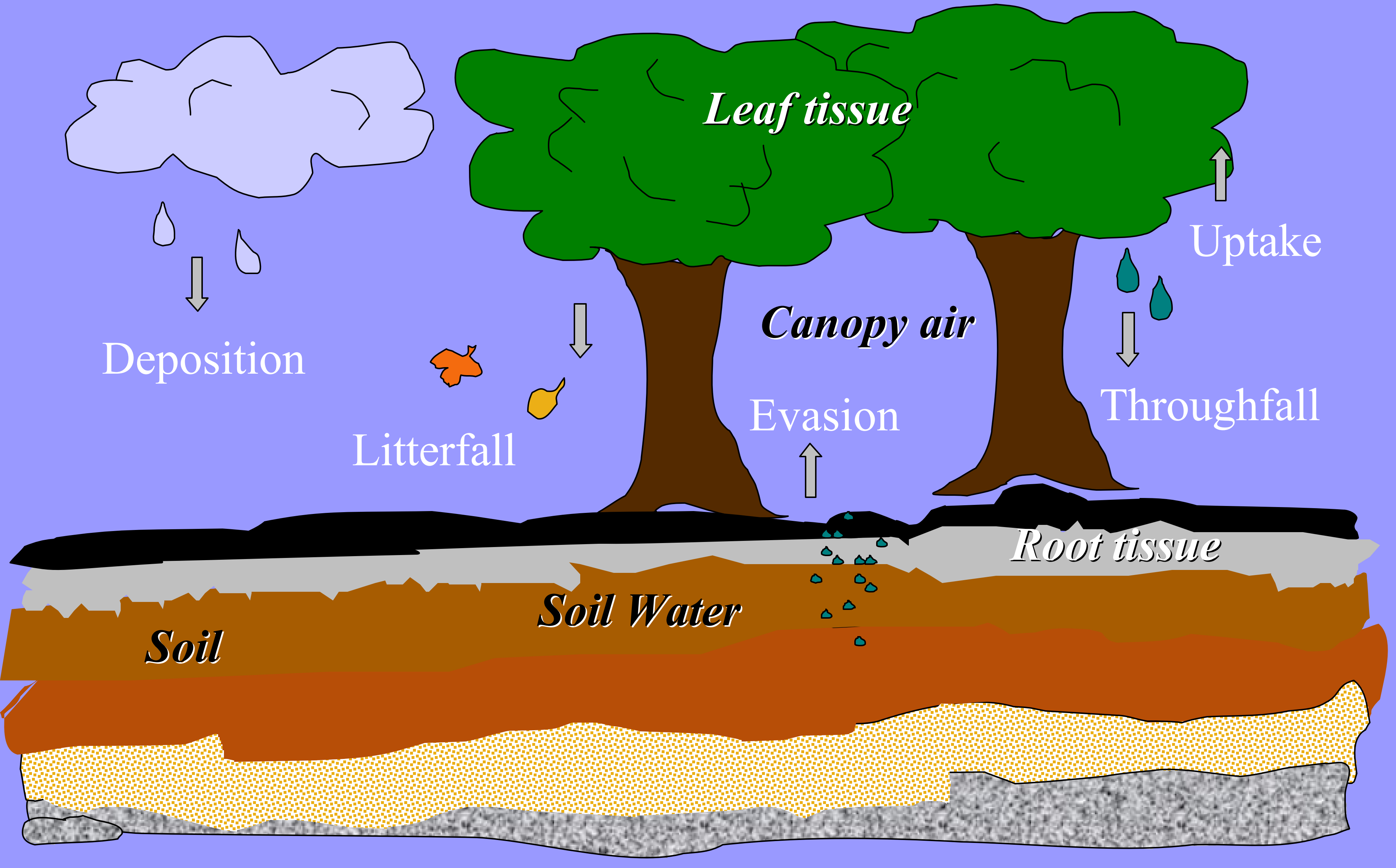


Propose 10 intensive sites in the U.S.

- **Each intensive site would have 15-20 cluster sites surrounding it**
- **Intensive sites would be chosen to represent the different ecoregions of the U.S.**

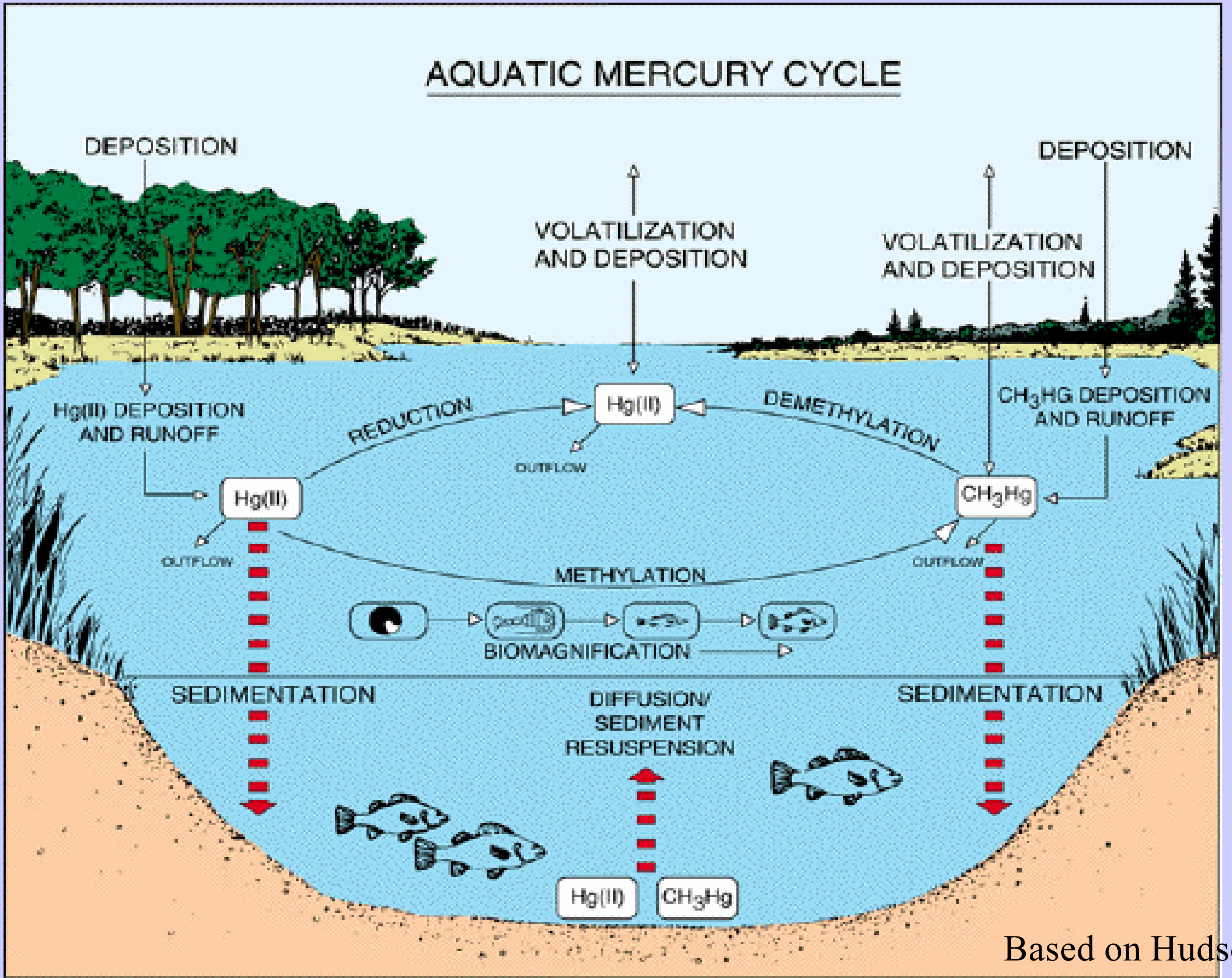
At Intensive Sites: Total Ecosystem Hg Deposition

Wet, Dry, Throughfall, Litterfall, Uptake by Plants



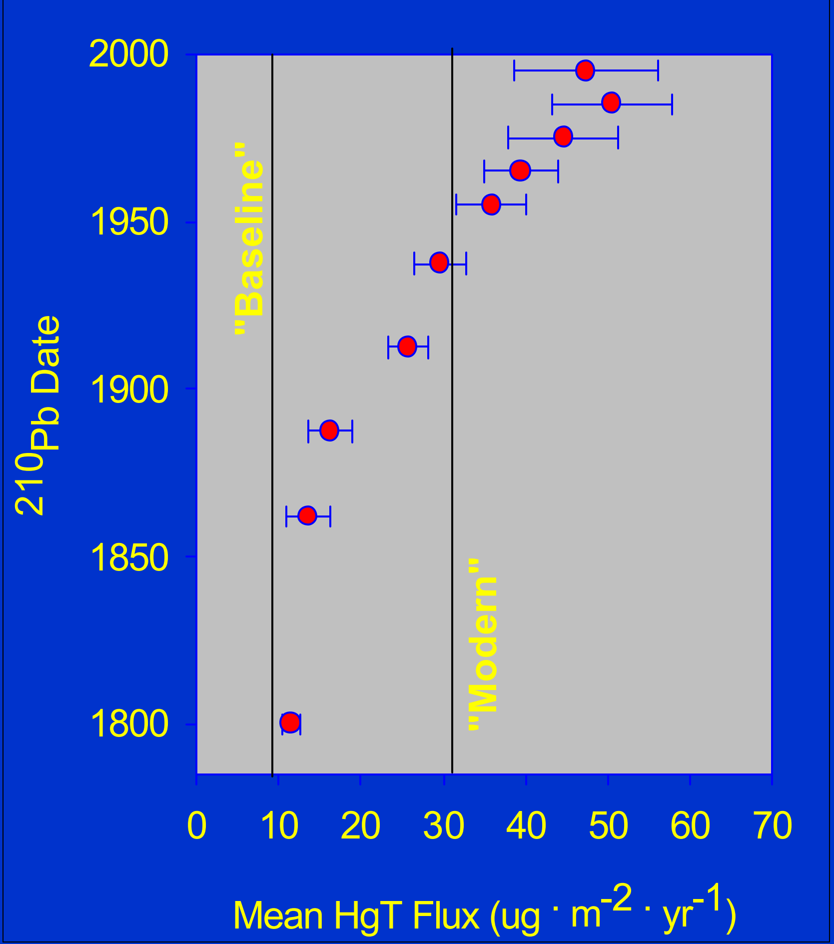
Water and Sediment:

Mercury cycling and the formation of methylmercury in aquatic systems is complex and to understand these processes fully requires the measurement of Hg speciation and other variables



Based on Hudson et al. (1994)

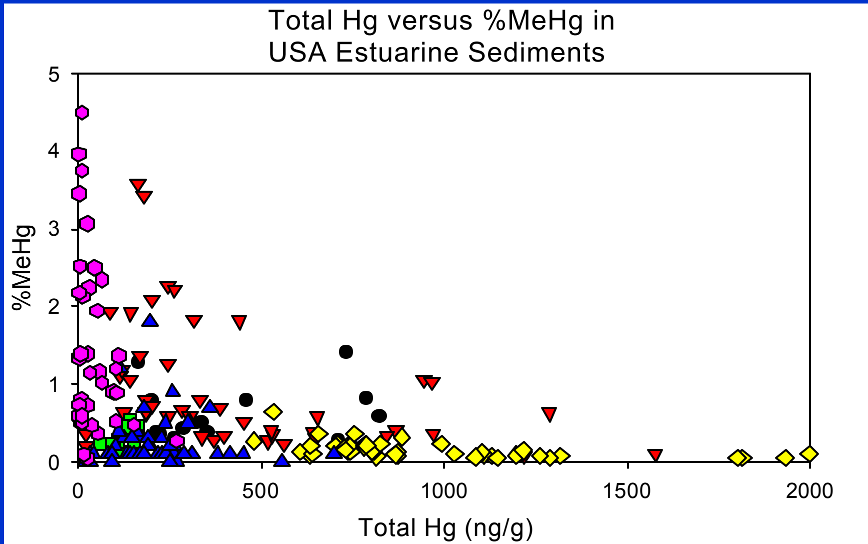
From Kamman and Engstrom (2002)



Sediment cores are good indicators of relative change over time of total Hg input

There is not a strong relationship between total Hg and MeHg and thus it is insufficient to only measure total Hg concentrations in sediments, or in the water.

%MeHg can give some indication of relative bioavailability



The Indicators

Air & Deposition

- Continuous speciated atmospheric concentrations
- Total wet and dry Hg deposition & flux
- Total Hg weekly wet deposition/flux
- Total and methyl Hg in throughfall
- Total and methyl Hg in litterfall
- Total Hg in snowpack
- Mercury evasion/flux
- Watersheld inputs/yields

Water and Sediment

- Total and MeHg in soil
- Forest floor surveys
- Total and MeHg, %MeHg in sediments (seasonal)
- Instantaneous sediment methylation/demethylation rate
- Total and methyl Hg accumulation in cores
- Total and methyl Hg in surface water (seasonal)
- Water column Hg & MeHg profiles

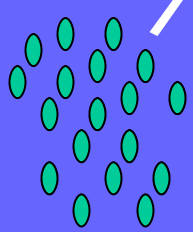
Indicators in green would be monitored at intensive sites only

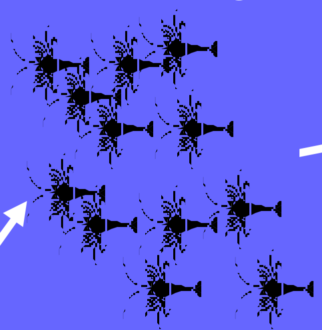
Mason et al. (2005)
Harris et al. (2007)

Aquatic Biotic Indicators:
Methylmercury Accumulation in Fish

Piscivorous fish only provide an indication of long-term change

Phytoplankton and zooplankton concentrations change too rapidly for them to be useful indicators for long-term change





Yearling fish are good indicators of yearly changes in concentration

Estuarine invertebrates are good indicators for changes that would be occurring in coastal ecosystems

Wildlife

* Need different species for across habitat comparisons
* For different types of ecosystems
*To monitor short-term versus longer-term changes





Sample blood, eggs, feathers, fur etc

The Indicators, cont.

Aquatic Biota

- Total and MeHg in phyto/zooplankton
- Total and MeHg in estuarine benthic invertebrates
- Total and methyl Hg in whole prey fish (YOY)
- Total Hg in muscle of piscivorous fish

Indicators in green would be monitored at intensive sites only

Wildlife

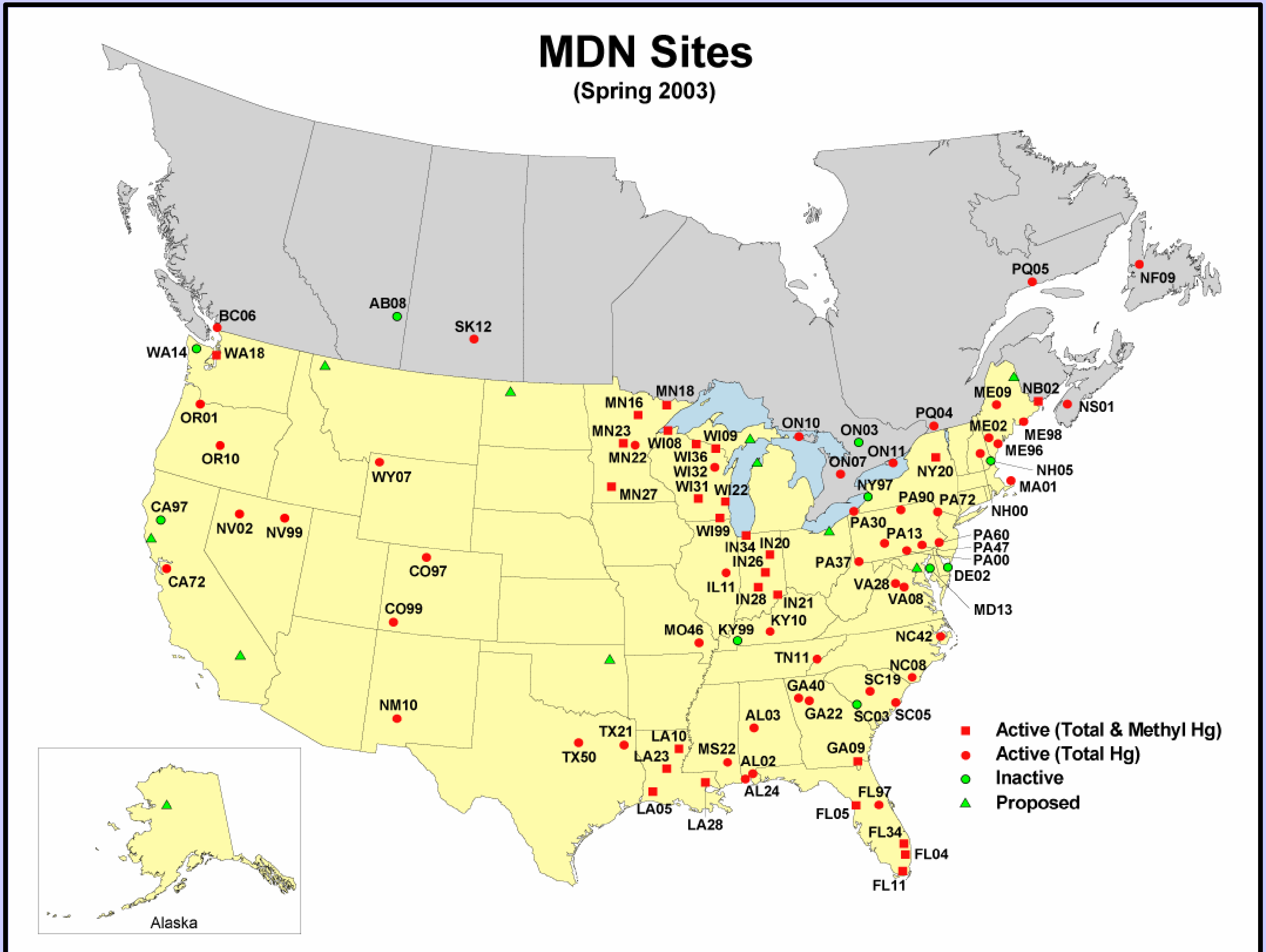
Total Hg in blood, feathers, eggs (as appropriate)

Potential Indicator Species

- Comparison across habitats: Belted kingfisher
- Terrestrial: Racoon, Bicknell’s thrush
- Riverine: Mink
- Lake: Common loon
- Lake/coastal: Herring gull, Common tern
- Wetland: Tree swallow
- Estuarine: Sharp-tailed & seaside sparrows
- Marine nearshore: Harbor porpoise
- Marine off-shore: Storm petrel

Mason et al. (2005)
Harris et al. (2007)

Use should be made of existing sites and monitoring networks such as the NADP/MDN Network

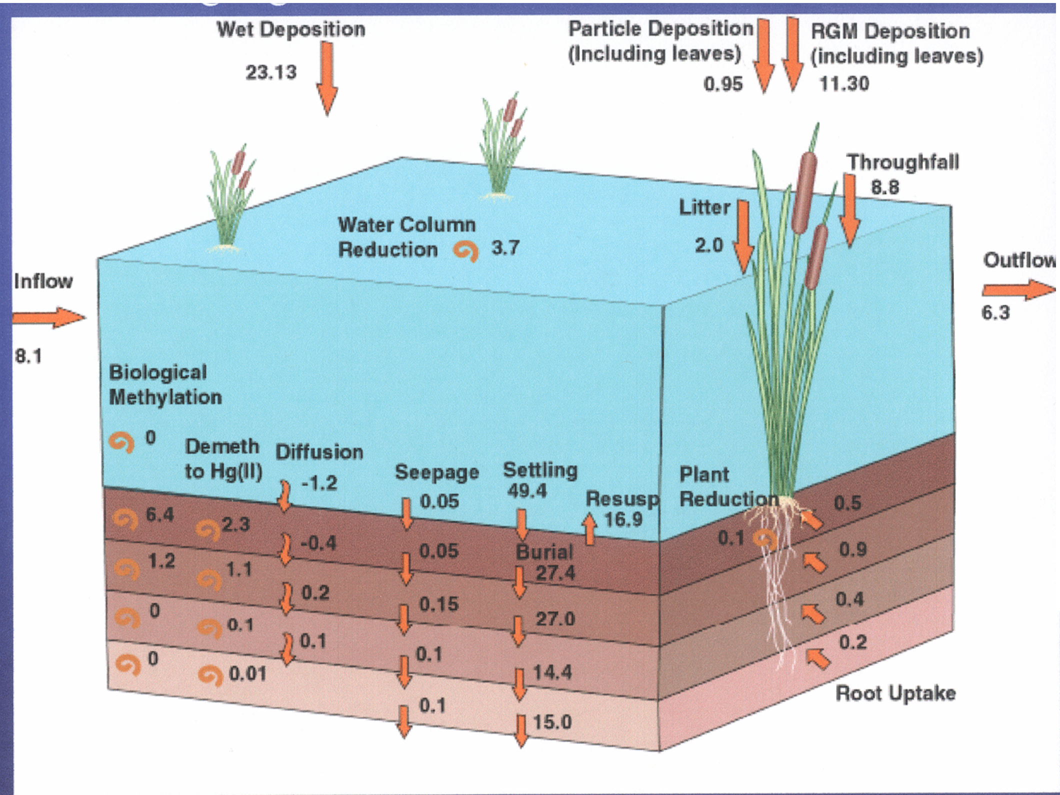


From NADP Website

Models

- Atmospheric fate and transport and deposition, exchange at the air-biosphere interface
- Watershed processing and transport to aquatic systems
- Biogeochemical cycling, including net methylation, and ecosystem bioaccumulation
- Health risk assessment
- Global, regional and local scale models are needed

Biogeochemical models are essential for integration



Models of mercury cycling within the aquatic system are complex and are dependent on the parameterization of a few key factors, such as methylation rate, that are not well known. For example, for the Everglades, sediment burial is the major sink for Hg, and is a crucial parameter in determining net Hg methylation.

The data shows relatively high variability. The model predictions match the average data within a factor of two. This may not be a sufficiently accurate for regulatory purposes, or to determine the impact of reductions in loading on fish MeHg

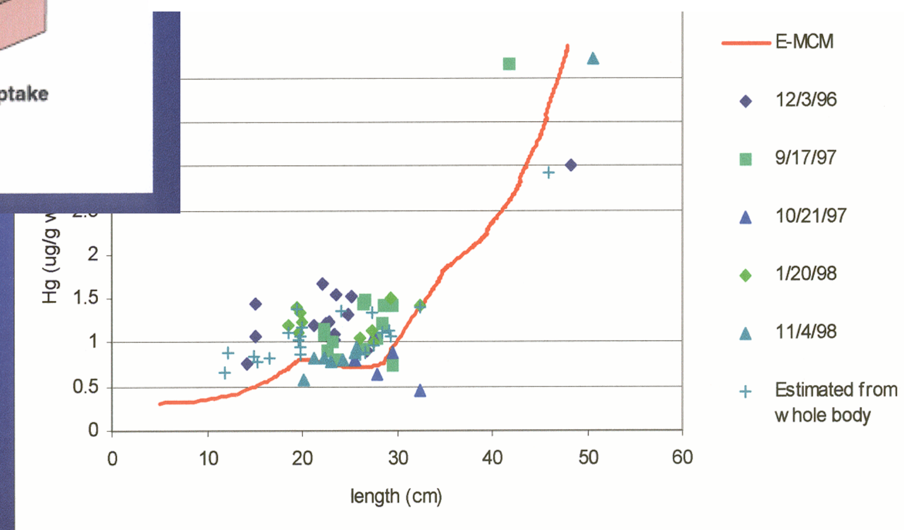


Figure 20. Predicted long-term methylmercury concentrations in largemouth bass in WCA 3A-15 for calibration with current atmospheric Hg(II) deposition = 35.32 mg/m2/yr. Observations: Lange et al., unpublished data

Taken from Harris, 2005

While the response in some ecosystems will be rapid, models indicate that the response time for large ecosystems, and especially for the ocean, will be slow given the relative low input compared to the reservoir size.

TABLE 2.1
Response of 4 hypothetical lake ecosystems to changes in national Hg emissions. (Note that these concepts are also relevant for river and coastal ecosystems.)

Ecosystem type	Urban lake	Forest lake	Forest lake	Forest lake
Hg deposition	High	Moderate	Moderate	Low
Hg sources	Local, regional, global	Regional, global	Regional, global	Global
Airshed response	High, rapid	Moderate, rapid	Moderate, rapid	None
Hydrologic flowpath	Short-circuited	Shallow	Deep	N/A
Watershed response	Rapid	Moderate	Slow–none	None

Harris et al. (2007); Sunderland and Mason (2007); Strode, unpubl.

Concluding Remarks

- Change is already occurring, so programs should be initiated ASAP
- Implementing a plan of this nature would allow detection of change in deposition as well as its impact across diverse ecosystems
- An overall monitoring strategy is coupled with focused and definitive study (intensive sites, modeling studies) at a small number of locations to provide enough information to make proper longer-term predictions
- Modeling studies will allow the extrapolation across ecosystems and allow scenario projection. However, model accuracy requires detailed information with spatial and temporal coverage